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Use and Limitations of Electrochemical Techniques for Investigating Microbiological Corrosion *

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ABSTRACT

Electrochemical techniques such as: corrosion and critical pitting potential measurements, direct current potentiostatic and potentiodynamic polarization, linear polarization resistance, split-cell current measurements, electrochemical impedance, electrochemical noise, and electrical resistance probes are evaluated for use in investigating microbiologically influenced corrosion. Examples are given to illustrate the capabilities and limitations of each technique.

KEY WORDS: electrochemical, microbiologically influenced corrosion, testing

INTRODUCTION

It is widely recognized that microorganisms attach to, form films on, and influence the corrosion of metals and alloys immersed in natural aqueous environments. The microorganisms influence corrosion by changing the electrochemical conditions at the metal surface.[1] Theoretically, these changes may have many effects, ranging from the induction of localized corrosion, to a change in the rate of general corrosion, to corrosion inhibition. In every case, however, the process of corrosion is electrochemical, and electrochemical techniques can be useful, if carefully applied, in the investigation of corrosion under both aerobic and anaerobic conditions.

Recently, there has developed a greater recognition of the complexity of the microbiologically influenced corrosion (MIC) process. MIC is rarely linked to an unique mechanism or to a single species of microorganisms. At the present state of knowledge, it is widely accepted that the growth of different microbial species within adherent biofilms facilitates the development of structured consortia that may enhance the microbial effects on corrosion. Therefore, it is necessary to be careful in the interpretation of data from electrochemical techniques applied to systems in which the complex and often poorly understood effects are derived from the presence of microorganisms and their extracellular polymeric substances (EPS, or simply, "slime").

MIC depends on the complex structure of corrosion-product and passive films on the metal as well as on the structure of the biofilm. Unfortunately, electrochemical methods have sometimes been used in complex electrolytes, such as microbiological culture media, where the characteristics and properties of passive films are not fully understood. It has to be kept in mind that microbial colonization of passive metals can drastically change their resistance to film breakdown by causing localized changes in the type and concentration of anions, pH, oxygen gradients and inhibitor levels at the metal surface. These changes can be expected to result in important modifications in the electrochemical behavior of the metal and, accordingly, in the electrochemical parameters measured in laboratory experiments.

Laboratory studies have often been made without considering the possibility of a change in the passive film on the metal after microbial colonization. If such a change taking place during the course of an experiment is not recognized, it can dramatically reduce the usefulness of conventional electrochemical techniques. However, the use of appropriate electrochemical methods, coupled with careful experimental design and characterization of the microbiological, electrochemical, and metallurgical components of the

system can lead to a better understanding of the mechanisms involved in many cases of MIC.

OPEN-CIRCUIT CORROSION POTENTIAL

The open-circuit potential (or corrosion potential) of a corroding metal can be measured by determining the voltage difference between that metal immersed in a corrosive medium and an appropriate reference electrode. The magnitude and sign of the corrosion potential are functions of the metal itself, as well as the composition, temperature, and hydrodynamics of the electrolyte. In reporting this potential, indicating the magnitude of the voltage, its sign, and the kind of reference electrode used is important. The open-circuit potential may be measured using a potentiometric circuit, a high-impedance voltmeter, or an electrometer. These instruments are capable of accurately measuring small voltages without drawing enough current to polarize (i.e., change the potential of) either the reference electrode or the test electrode.

Because of its simplicity, measurement of the corrosion potential has been used in MIC studies for many years.[2-4] The measurement of open-circuit potential vs time was used by these authors to assess the electrochemical behavior of steel specimens immersed in cultures of sulfate-reducing bacteria (SRB). The initial immersed in cultures of sulfate-reducing bacteria (SRB). The initial potential decay observed in these media was attributed to cathodic depolarization of the steel electrode by Hadley,[2] or to enhancement of the anodic process by Wanklyn and Spruit.[3] Some years later, in similar experiments, Horvath[4] attributed the steady-state corrosion potential, after an initial decrease, to the formation of a semiprotective film of iron sulfide. These early uses of open-circuit potentials for studying corrosion induced by SRB were limited by the lack of complementary measurements. However, sudden changes (usually in the active or negative direction) in a plot of potential vs time proved to be useful for detecting the initiation of accelerated attack due to bacteria.

Corrosion potential measurements were also used to study the behavior of 2024 (UNS[(1)] A92024) aluminum alloy in the presence of aggressive metabolites produced by *Hormoconis resinae* (*H. resinae*) during the degradation of hydrocarbon chain molecules[5] (Figure 1). Using differences in the variation of the open-circuit corrosion potential with time, it was possible to distinguish between the typical behavior of a passive metal (constant potential) and the onset of localized pitting (strong oscillations). Microscopic observation of the samples indicated the presence of pits and general corrosion zones, confirming the results suggested by the electrochemical measurements.

Several papers have been published recently using variations in the measured corrosion potential with time to follow the effects of developing biofilms on the corrosion of stainless alloys in seawater.[6-12] These data show that the corrosion potentials of a variety of stainless alloys are often shifted in the positive direction (ennobled) in the presence of a biofilm.[6-10] One set of representative data of this type[9] is shown for alloy C-276 (UNS N10276) in Figure 2. Other data[11,12] have shown that ennoblement does not always occur, particularly when localized crevice corrosion or pitting takes place.[11] Similar data show that potential ennoblement does not occur on alloys such as 70/30 copper-nickel that do not form passive films when immersed in seawater.[13] Such data as that cited above is most useful in determining how corrosion is influenced by the presence of a biofilm when it is accompanied by similar data obtained under identical experimental conditions but without the microorganisms. Several techniques for removing the organisms from natural waters have been discussed in the literature.[11,14]

[(1)]UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE) and cosponsored by the American Society for Testing and Materials (ASTM).

REDUCTION-OXIDATION (REDOX) POTENTIAL

Another potential useful in predicting whether or not a given metal will suffer an increase in corrosion due to microorganisms is the reduction-oxidation (or redox) potential of the environment. This refers to the relative potential of an electrochemical reaction under equilibrium conditions where there is no net flow of electrical current. The redox potential of an environment such as moist soil is actually the equilibrium potential of the oxygen reaction as measured on a platinum electrode immersed in the soil. At the redox potential, the rates of oxidation and reduction at the platinum surface are assumed to be equal, and the redox potential itself is a function of the oxygen concentration, temperature, and pH of the soil. At a given temperature and pH, the redox potential of any natural aqueous environment becomes more negative (or active) with decreasing dissolved oxygen concentration.

Redox potential measurements have been used frequently in microbiology to assess the suitability of a given environment for the growth of the anaerobic SRB. Since these organisms grow only in the absence of oxygen, they require an environment with an active, or oxygen deficient redox potential (generally less than −400 mV$_{SHE}$). In the MIC literature, the redox potential has been used to estimate the aggressiveness of soils towards buried metals, and it has been considered by some authors as the most significant factor in assessing the aggressiveness due to SRB.[15] However, the combined use of several parameters such as electrical resistivity, redox potential, and water content of the soils seems to be more adequate.[16] When measuring the redox potential for an electrochemical reaction such as oxygen reduction:

$$1/2 O_2 + H_2O \rightleftharpoons 2OH^- - 2e^- \qquad (1)$$
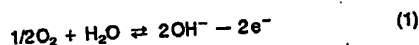
a concurrent measurement of pH is necessary since the measured potential is a function of both oxygen concentration and soil pH, as indicated by the Nernst equation corresponding to Reaction (1) above:

$$E = E^\circ - \frac{RT}{2F} \ln \frac{[OH^-]^2}{P_{O_2}^{1/2}} \qquad (2)$$

In contrast to the use of redox potentials for characterizing the aggressiveness of soils toward steel is their use for characterizing the corrosiveness of aerobic microbial culture media toward metals and alloys. Strictly speaking, the redox potential is only defined for an electrochemical reaction under equilibrium conditions. Such conditions may be found in sterile culture media, but are not usually encountered in living systems, where the organisms are actively metabolizing. Nevertheless, steady-state conditions do occur in active microbial cultures, and the redox potential measured under these conditions can provide useful information on the characteristics of that environment and any changes it undergoes as a result of bacterial metabolism. Unlike the active (or negative) redox potential that signals corrosive conditions for steel, a noble (positive) redox potential usually indicates conditions favorable for corrosion under aerobic conditions. This is particularly true for active-passive metals that corrode by localized pitting. For such metals, the combination of a noble redox potential for the environment, with a noble corrosion potential and an active (negative) pitting potential can indicate high aggressiveness of that environment for the alloy. Note when making such measurements that the immersion time of the platinum electrode must be short enough to avoid colonization by the microorganisms. Otherwise, the measured value will not be representative of the bulk solution.

As an example, the redox potentials of different culture media were used in association with Pourbaix diagrams to predict the probable behavior of aluminum, nickel, and zinc in those media.[17] The growth of aerobic organisms produces complex modifications
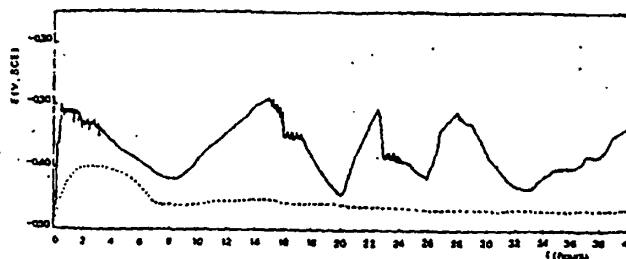
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FIGURE 1. Open-circuit potential vs time[5] for 2024 aluminum alloy in (1) Hormoconis resinae culture, pH 4.0; E_{redox} = -0.27 V_{SCE} and (2) sterile medium containing 13 mg per 1000 mL dodecanoic acid at pH 7.0.
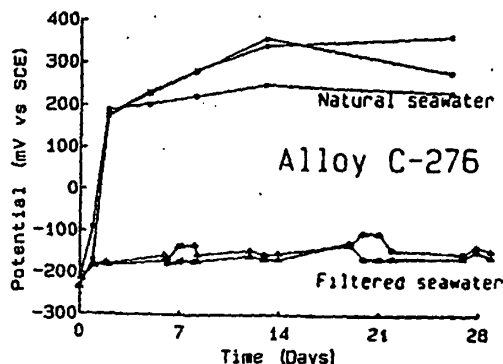

FIGURE 2. Open-circuit potentials of alloy C-276 during biofilm formation in natural and filtered seawaters.[9]

In these systems through oxygen consumption, the production of metabolites, and the incorporation of products of cellular lysis in the medium.[18] The consumption of oxygen produces a decrease in the cathodic reaction rate, favoring protection of the metal, but the production of acid or oxidizing substances counteracts the oxygen depletion producing a net increase in the cathodic rate. Therefore, the influence of pH and oxygen levels on the breakdown of passivity of aluminum can be used together with redox potential variations in understanding the changes produced in the medium during microbial growth in fuel water systems. The more noble (positive) values of the redox potentials measured in cultures of *H. resinae* and *Pseudomonas aeruginosa* (Table 1) as compared to those in sterile media are explained by an increase in the amount of reducible species existing in the solution (protons or metabolic products).

Noble redox potential values along with noble corrosion potentials and active pitting potential (E_p) values can explain the aggressiveness of *H. resinae* for aluminum. In fuel/water systems where different species of bacteria and fungi often grow together, the redox potential can be useful in studying the role played by each species in modification of the medium. In the case of active--passive metals like aluminum and its alloys, where a localized form of attack is predominant, the use of redox potentials together with an electrochemical parameter, such as the corrosion potential or the E_p, can be of great importance in assessing whether the oxidizing conditions of the medium can reach the values needed to initiate localized corrosion.[18]

DIRECT CURRENT POLARIZATION METHODS

The current-potential (Evans) diagram is a graphical method for demonstrating the relationship between the reversible potentials of anodes and cathodes and the polarization behavior of anodic and cathodic reactions. Both reactions are represented as linear curves that converge and intersect on a potential (E) vs log I plot. The intersection point corresponds to the corrosion potential and the corrosion current. If these curves could be measured directly, then the corrosion current could be determined, and it could be converted to the instantaneous, average uniform corrosion rate of the metal through Faraday's law.

Unfortunately, neither the reversible potentials nor the corrosion current can be measured directly. Thus, indirect methods must be used, and a large number of such methods have been developed. The general procedure is to use a potentiostat in conjunction with a reference electrode to measure the corrosion potential, and then to polarize the specimen from the corrosion potential, in either the active (cathodic) direction, or the noble (anodic) direction, or both. Depending upon the method to be used, these polarizations may be large (several hundred millivolts) or small (e.g., 10 to 20 mV), and they may be done by controlling either the applied potential or the applied current. Polarizations may also be done either quasi-statically in discrete steps at some appropriate time interval (25 mV every 5 minutes is common) or dynamically at a constant scan rate. The utility and limitations of several of these techniques for investigating MIC will now be discussed.

Tafel Polarization

Increasing the applied potential in the noble direction away from the corrosion potential causes the specimen to behave as an anode. The anodic current increases with increasingly noble potential, giving rise to the measured anodic curve. In theory, both the cathodic and the anodic curves should be linear when the applied potential, V, is plotted vs the logarithm of the current density, i (A/cm^2), and the two curves should intersect at a point representing the corrosion potential and the corrosion current density. The measured log current vs potential curves both deviate from linearity in the vicinity of the corrosion potential; nevertheless, both often contain linear segments, sometimes referred to as Tafel regions. Extrapolating the linear segments of either the anodic or cathodic curves back to the corrosion potential yields the corrosion current density (Figure 3). Strictly speaking, such extrapolations give a valid value for the corrosion current density only when the linear Tafel region extends for several decades of current. Extrapolations from the linear segment of the cathodic curve are generally preferred, since the latter is often easier to measure experimentally and is less affected by corrosion-product and biological films. Sev-

TABLE 1
Redox Potentials for Different Cultures of Microbial Contaminants of Kerosene Fuels[18]

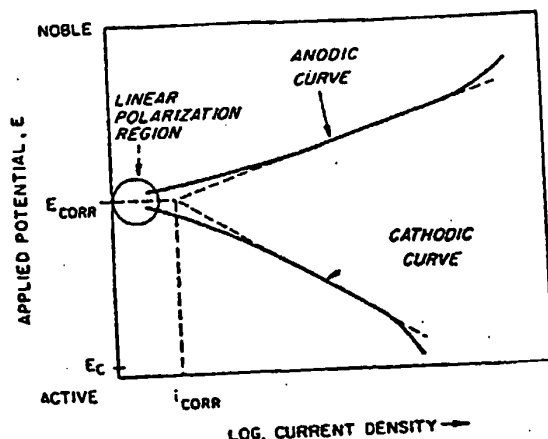| Microorganisms	pH	E_H (mV$_{SHE}$)	Incubation Time (days)
H resinae	4.8	−420	30
H resinae	3.2	−328	90
H resinae	2.6	−288	180
Ps. aeruginosa II	5.1	−438	30
Ps. aeruginosa I	6.2	−438	30
Candida sp.	6.0	−426	30
Candida sp. + Ps. aeruginosa	4.5	−333	30
Ps. aeruginosa II + H resinae	4.5	−323	30
Sterile medium	7.0	−480	

FIGURE 3. Measurement of i_{corr} extrapolation.

eral practical procedures are described in the corrosion literature for measuring the corrosion current density by the extrapolation technique, including both potentiostatic and galvanostatic procedures. The corrosion current density can be converted to a corrosion rate according to the relationship:

$$R = 0.13\ i_{corr}\ K/p \qquad (3)$$

where R is the corrosion rate in mm per year, i_{corr} is the corrosion current density ($\mu A/cm^2$), K is the equivalent weight of the metal, and p is the metal density (g/cm^3). The extrapolation technique for measuring i_{corr} is dependent on both a steady corrosion potential and the ability to identify the linear Tafel region. Electrolytes in which more than one reduction reaction take place or in which concentration polarization occurs, exhibit less distinct linear regions. This greatly decreases the validity of the extrapolated values. These disadvantages can sometimes be overcome by the use of the linear polarization resistance technique, which will be described later. For systems in which the corrosion potential drifts or fluctuates with time (e.g., the 300 series stainless steels in natural seawater), Tafel polarization measurements are nearly meaningless.

Controlled-current (galvanostatic) polarization studies have been used for several decades in the study of anaerobic corrosion of iron by SRB. Booth and Tiller[20] used anodic and cathodic polarization curves of mild steel in the presence of different strains of SRB to ascertain the effect of the enzyme hydrogenase on ca-

thodic depolarization of the metal. These results represented the initial attempt to apply external polarization to an electrode in order to identify the basic mechanisms of corrosion induced by SRB. Later, other authors measured cathodic polarization curves for mild steel in sterile medium containing either suspensions of iron sulfide[21] or dissolved hydrogen sulfide[22] in an attempt to demonstrate that cathodic depolarization can be enhanced by the presence of those chemical species. More recently, polarization experiments have been used to assess variations in the polarizing or depolarizing effect of microorganisms with time under different experimental conditions or upon using different species of organisms[23,24] (Figure 4).

Although these methods have been used with considerable success as described above, several limitations should be kept in mind when applying them to biofilmed metals. First, the rather large polarizations required may change the electrochemical conditions at the metal surface in such a way as to be deleterious to microorganisms in the biofilm.[25] Thus, such measurements should not be made periodically during a corrosion experiment for the purpose of following the effect of biofilm development with time. They may, however, give useful information for research purposes if done once at the end of an experiment. Second, these measurements alone give no information on either the distribution of corrosion on the metal surface (MIC is usually localized) or on the relative contribution to corrosion of the biofilm as compared to that of other parameters. This means that careful work and well-designed control experiments are necessary if the results are to be useful, or even interpretable.

Potentiodynamic Sweep Techniques

The potentiodynamic techniques are most useful in characterizing, and sometimes predicting, the corrosion behavior for metalizing, and sometimes predicting, the corrosion behavior for metal–electrolyte systems in which the metal passivates by the formation of a protective (or passive) film. An idealized anodic polarization diagram for a passivatable metal, examples of which are aluminum, chromium, cobalt, iron, nickel, titanium, and their alloys, is shown in Figure 5 for an acidic electrolyte. Starting with the reversible metal potential, $E^r_{m/m}$ and moving upward on the diagram, one encounters first the active region, in which general corrosion takes place, with the corrosion rate increasing rapidly with potential. Upon reaching the primary passivation potential, E_{pp}, stable oxide films can form in aerated environments. Under these conditions, the metal is said to passivate, the corrosion current density drops from a maximum of i_{crit} to the very low passive current density, i_p, and one enters the passive region, in which the corrosion behavior is independent of potential. In electrolytes of more neutral pH (i.e., most natural aqueous electrolytes), the corrosion potential is already within the passive range, and the active current peak is not observed. At more noble potentials, the transpassive region is encountered, in which the corrosion rate increases once again, accompanied by oxygen evolution. Morphologically, corrosion at the beginning of the transpassive region usually takes the form of localized pitting. More will be said about measuring the potential at which pitting begins in the next section.

For a given corroding metal, the corrosion potential and corrosion current will be determined by the point at which the cathodic curve intersects the anodic curve as shown in Figure 6. Four generalized cases are illustrated, representing four cathodic reactions with different overvoltages. In Case 1, the active reversible cathode potential, E^r_1, causes the intersection to fall at point A in the active corrosion region with a high corrosion rate. In Case 2, the reversible cathode potential, E^r_2, is such that three intersections are possible at points B, C and D. This is an undesirable situation because the metal can jump with little or no warning from being passive to being active with a very high corrosion rate. Case 3 with reversible cathode potential, E^r_3, is the most desirable. This leads to an intersection in the stable passive region at point E. In

PRODUCED WATER   STERILE PRODUCED WATER
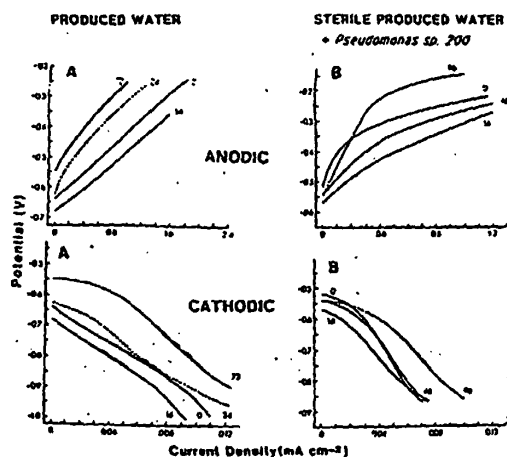   + Pseudomonas sp. 200

FIGURE 4. Polarization curves for mild steel in (a) produced water with natural microflora; (b) sterile produced water inoculated with Pseudomonas sp. 200. Numbers on curves indicate incubation times in hours.[24]
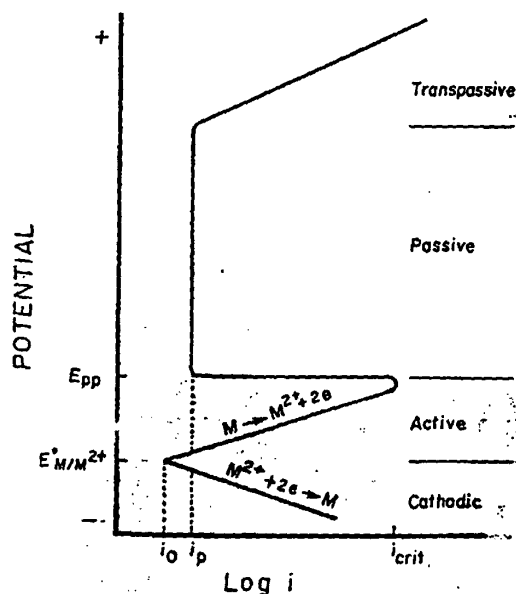

FIGURE 5. Schematic Stern diagram for anodic polarization of a "passivatable" metal.

Case 4, the cathode potential, E°_4, is noble enough to place the intersection at or above the start of the transpassive region, leading to localized corrosion. In Figure 6, the differences in overvoltage are depicted as if they were all thermodynamically controlled by the reversible cathode potential, E°. In practice, the differences in overvoltage could just as easily be caused by changes in the cathodic kinetics through variations in the exchange current density, i_o, Tafel slope, β, or passive current density, i_p, as shown schematically[26] by Dexter in Figure 7 for a stainless alloy in a neutral pH aqueous chloride environment.
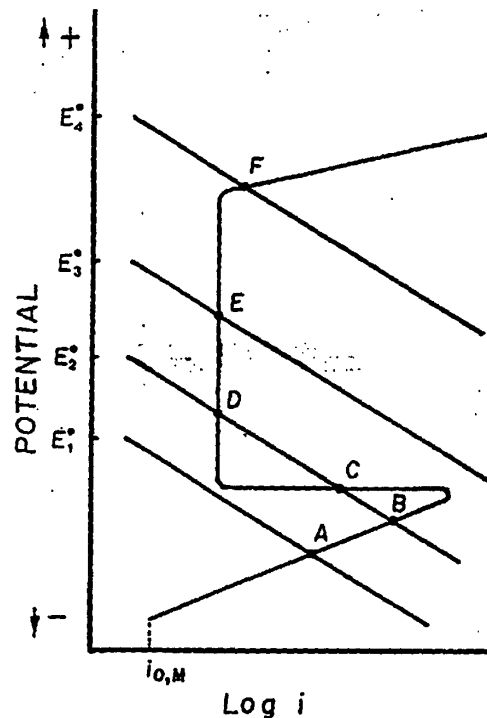

FIGURE 6. Schematic diagram of the intersection of four different cathodic curves with the anodic curve for a passivatable metal. Depending upon the cathodic curve, the corrosion potential may fall in the active (A), stable passive (E), unstable passive (B through D), or transpassive (F) regions.

In order for a metal to remain in stable passivity, it must have a low i_{crit}, an active E_{pp}, and a sufficiently noble start of the transpassive region to give an intersection of the anodic and cathodic curves similar to that in Figure 7 or Case 3 of Figure 6. This is the normal case for most austenitic, duplex, and super ferritic stainless alloys in aqueous electrolytes. The anodic and cathodic curves can then be affected sufficiently to disturb passivity by changes in solution chemistry, pH, temperature, hydrodynamics, or passive film formation tendencies. The presence of microorganisms on the metal surface either in the form of a distributed biofilm or discrete colonies can bring about such changes. It has recently been documented that a transition from Case 3 to Case 4 behavior can be caused by a general biofilm forming on stainless alloys immersed in seawater.[11] In that paper, the authors diagram the mechanism (Figure 8) as if the biofilm caused a change in cathode kinetics, but they admit that it could be related to either kinetics or thermodynamics. In systems where MIC is a possibility, it is important to know whether a change from Case 3 to Case 1, 2 or 4 behavior is likely. In many cases, the information needed can be obtained through potentiodynamic sweep techniques.

The basic techniques used in running these tests can be found in ASTM[2] Standard G3, Recommended Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing (1981), and G5, Polarization Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Polarization Measurements (1982). The rapid-scan potentiodynamic technique has also been reviewed recently by Siebert.[27,28] To per-

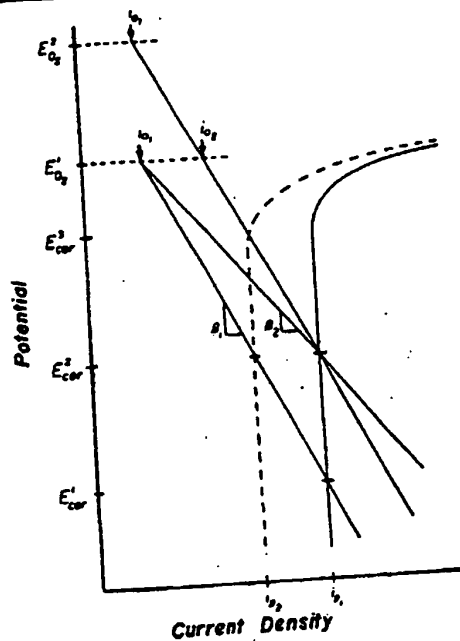[2]American Society for Testing and Materials (ASTM), Philadelphia, PA.

FIGURE 7. Schematic polarization diagram for a stainless alloy in a neutral chloride medium showing that changes in E_{cor} can result from either thermodynamic or kinetic influences on the cathodic overvoltage.[26]
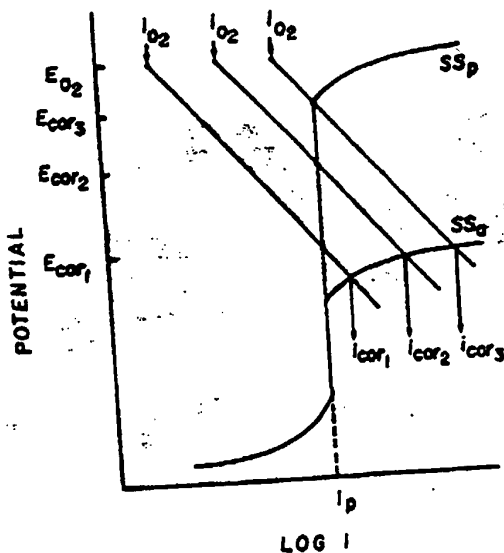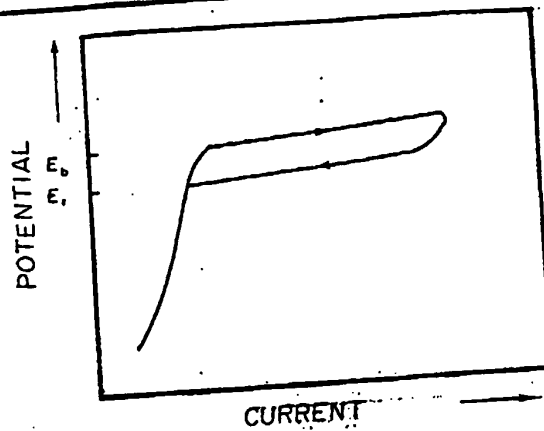

FIGURE 9. Schematic representation of anodic polarization curves for a metal immersed in a solution containing aggressive ions. Potentiodynamic (or potentiostatic) measurements would be conducted upward to determine E_b and backwards to determine E_r.

TABLE 2
E_b Values for Mild Steel[28]
in Postgate C Medium Without Fe(II) Under Various Experimental Conditions[(A)]

Additions to Sterile Medium	pH	E_b ($\pm 0.03\ V_{sce}$)
None	8.0	−0.21
None	7.0	−0.23
3% NaCl	8.0	−0.37
3% NaCl + V. alginolyticus	7.8	−0.43
3% NaCl + V. alginolyticus + 10^{-3} M Na$_2$S	7.5	−0.51
3% NaCl + V. alginolyticus + SRB	7.3	−0.60

(A)Incubation for bacterial cultures was 4 days.

FIGURE 8. Schematic diagram of the effect of an increase in cathodic kinetics (through i_o) on a stainless alloy, SS$_a$, having little resistance to localized corrosion initiation and on a more resistant stainless alloy, SS$_p$.

form the test, one usually starts at either the steady-state corrosion potential, or at a potential several hundred millivolts negative to that, and sweeps up through the corrosion potential and into the passive and transpassive range, then reversing the scan direction, returns to the corrosion potential or to the starting potential. The entire test may consist of one or more such cyclic sweeps.

One of the main experimental variables that can be manipulated is the sweep rate. Sweeping a range of potentials in the anodic (more electropositive direction) at a relatively high scan rate of 60 V/h is used to indicate regions where intense anodic activity is likely. Slower sweep rates of about 1 V/h are used to document regions in which relative inactivity is likely. The rapid sweep has the object of minimizing film formation so that the currents observed relate to thin-film or nearly film-free conditions. The objective of a slow sweep rate experiment is to allow time for filming to occur. Slow scan rates provide for maximum stability of the metal surface, but increase the chance for changes in the environment or in biofilms at the potentials furthest from the corrosion potential. High scan rates disturb the steady-state reaction conditions at the metal surface, but better maintain the stability of the environment. At any scan rate, the large applied potentials often used in potentiodynamic experiments may disturb the organisms in the biofilm, as was the case for Tafel polarization above. Thus, the same caution against performing the polarization during the middle of a long-term experiment applies here. MIC involves the action of relatively fragile organic and biological films that are affected by

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pH and the concentrations of oxygen and hydrogen at the metal–film interface. Thus, the scan rates discussed above, which can affect these variables, are very important when applying potentiodynamic techniques to MIC systems. Rapid scan rates can be used to develop a database for possible expected corrosion regimes for the film-free metal in a given environment. Intermediate scan rates may be selected to correspond to a particular biofilm formation rate, while very slow scan rates may be selected for measurements of the relatively steady-state conditions in the presence of a mature biofilm. Thus, no single scan rate is appropriate for use in all MIC investigations.

Two useful parameters that can be determined potentiodynamically (or potentiostatically) are the breakdown potential, E_b, (defined further below) and the repassivation potential, E_r. These correspond to the potentials associated with pit formation and repassivation during a cyclic potential sweep as shown in Figure 9. An example of the use of E_b values, measured with the potentiodynamic method was given by Gaylarde and Videla.[29] The experimental data in Table 2 show the effect of their different experimental conditions on E_b. These data demonstrate that addition of a marine strain of *Vibrio alginolyticus* to a sterile 3% NaCl medium was able to shift the E_b of mild steel markedly in the negative direction, making pit initiation more likely. Further additions of 10^{-3} M Na_2S and SRB both produced additional negative shifts in E_b, with the SRB additions giving the largest shift. SEM observations of biofilms formed on mild steel samples in the presence of *V. alginolyticus* or in the presence of a mixture of *V. alginolyticus* + SRB gave additional support to the electrochemical evaluation of E_b values and clearly demonstrated the importance of microbial consortia in the enhancement of corrosive effects.

Determination of Pitting Potentials

Microorganisms often stimulate localized forms of corrosive attack, such as pitting, depending on the passive film forming and repairing capabilities of the metal or alloy. Different methods for determining characteristic pitting potential values can be useful in defining the tendency of microorganisms to accelerate pitting in a given metal/solution system. The general term *pitting potential* is used in the literature to mean a variety of different electrochemical parameters related to the onset of pitting corrosion. The numerical value obtained for the pitting potential depends strongly on the details of the experimental technique used to measure it, and strictly speaking, the value measured by each of these techniques should be called by a different name. As an example, the *critical pitting potential*, E_{cpp}, is usually defined as the most noble potential at which the passive current density remains stable and pits do not nucleate on a crevice-free surface. This value is measured potentiostatically in the laboratory under carefully controlled conditions. If measured carefully, E_{cpp} is independent of the geometry of the specimen and the test apparatus.

In contrast is the *breakdown potential*, E_b, defined as the potential at which the anodic polarization curve shows a marked increase in current, leading to breakdown of the passive film and pit initiation. This value is usually measured by the potentiodynamic polarization sweep techniques discussed in the previous section, and the value obtained depends on both the sweep rate and experimental geometry.

It is beyond the purpose and scope of this paper to discuss the great variety of experimental techniques for measuring pitting potentials and the validity of the data obtained. Such matters have been discussed extensively in the literature[30,31] to which the reader is referred. The purpose of this paper is to assess the usefulness of pitting potential measurements in general for investigating MIC, and, except where stated otherwise, the symbol, E_p, will be used to mean any generic pitting potential measurement.

While no information exists in the literature regarding field studies, it has been shown in several laboratory studies[18,29,32] that the presence of corrosion causing microorganisms decreases (makes less noble) the E_p values of several metals and alloys in varied media. One of these studies[34] showed the effect of SRB and sulfide contamination on the potentiostatic anodic polarization curves of type 1020 (UNS G10200) steel in anaerobic artificial seawater (Figure 10). The additions of SRB and sodium sulfide seawater alone. These experimental results suggested that, in seawater alone. These experimental results suggested that, since the SRB behaved in a similar manner to chemically added sulfide, the action of anaerobic bacteria on the corrosion of mild steel was a consequence of metabolic sulfide production. In addition, the breakdown of passivity was accomplished more easily in deaerated solutions where lower levels of sulfides were needed.

Induction Time for Pit Nucleation

The time it takes to form the first pit on a passive metal exposed to a solution containing aggressive anions (e.g., chlorides or sulfides) is called the *induction time* for pit initiation, τ. At a constant potential noble to E_p, the induction time depends on chloride ion concentration. For a given metal, τ decreases as either the chloride concentration or the potential or both are increased. However, τ also depends on the quality of the passive film and on the experimental conditions.[31] Usually, τ is determined by recording changes in the current density vs time at a constant applied anodic potential. When pitting is initiated, there is a sudden increase in current, and the time elapsed between potential application and current increase is a measure of τ.

This parameter has been used to assess the effect of one of the primary metabolic products of *H. resinae* on the corrosion behavior of 2024 aluminum alloy[35,36] as shown in Figures 11 and 12. In these Figures, τ corresponds to the minimum in the current density vs time curves. Thus, in the 10^{-2} M sodium chloride solution of Figure 11, τ is greater than 20 s for a curve a at -0.55 V_{SCE} (the E_p value for 2024 aluminum alloy in 10^{-2} M sodium chloride solution), and it decreases with increasing applied potential in the neutral chloride solution, being less than 10 s in curve a and tial to between 5 and 10 s for curves b and c. In the 10^{-2} M sodium chloride + 10^{-2} M citric acid solution (Figure 12), the τ values are shorter than they were at the same three fixed potentials in the neutral chloride solution, being less than 10 s in curve a and too small to measure by this technique in curve c. These measurements suggest that *H. resinae* metabolites, such as citric acid, can play an active role in the electrochemical behavior of 2024 aluminum alloy. Any other acidic metabolite would be likely to have a similar effect.

Polarization Resistance Measurements

One of the electrochemical methods that has been applied to MIC studies over the last several years is the polarization resistance (or linear polarization resistance) technique. This method is based on the nature of the linear relationship between changes in the applied potential and the resultant current density, when the applied potentials are within about ± 10 mV of the corrosion potential. The technique is based on the assumption that the interface behaves as a simple resistor, whose magnitude is inversely proportional to the corrosion current.[37] The slope of the potential-current curve is approximately linear and has units of resistance. A number of commercial instruments are now readily available for linear polarization measurements. These instruments basically contain a test probe, reference and auxiliary electrodes, a current source, an ammeter, a voltmeter, and a display panel, and they are beginning to find increasing use in monitoring instantaneous corrosion rates in industrial plants.
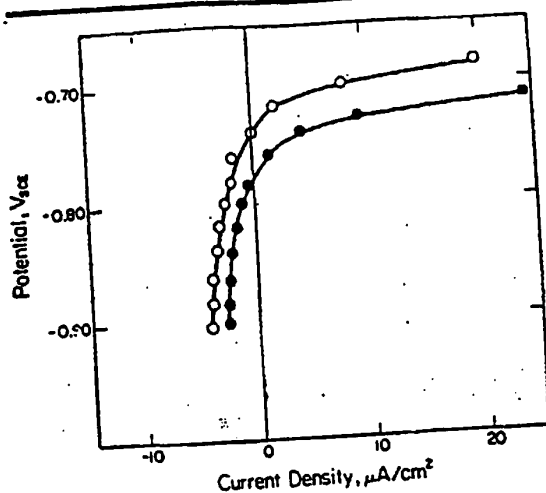
FIGURE 10. *Potentiostatic polarization curves for type 1020 steel in anaerobic artificial seawater[34] contaminated by SRB (o), at pH 7.8, total sulfides = 0.001 M and E_{redox} = −0.510 V; and in seawater with the addition of 0.001 M sodium sulfide (●).*
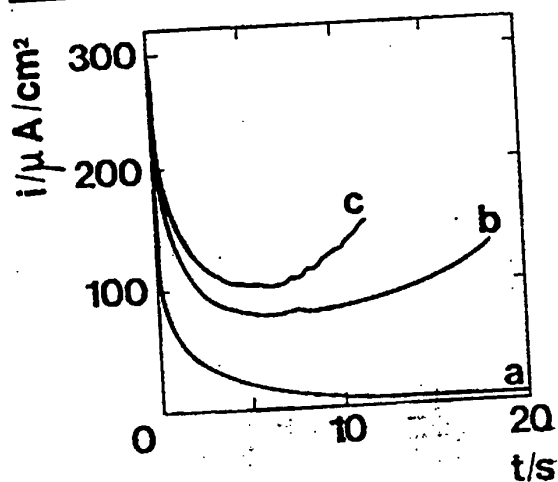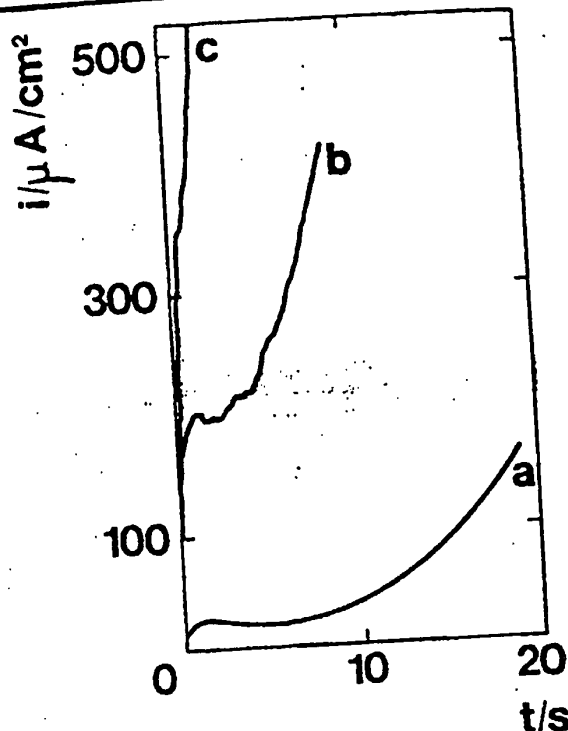

FIGURE 12. *Current transients at constant potential[36] recorded in 0.01 M sodium chloride + 0.05 M citric acid (pH 2.5). Potential was fixed at (a) −0.55 V; (b) −0.50 V; (c) −0.48 V.*
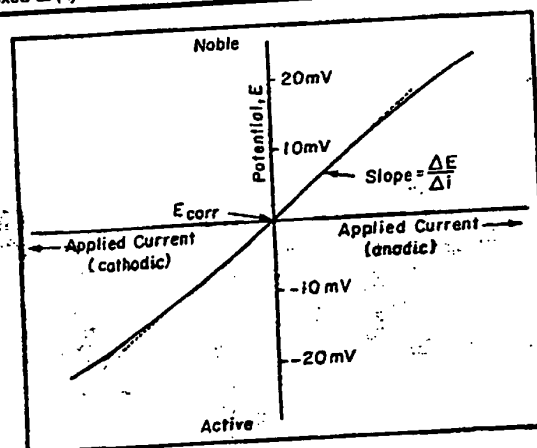

FIGURE 11. *Current transients at constant potential recorded in 0.01 M sodium chloride.[36] Potential was fixed at (a) −0.55V; (b) −0.50 V and (c) −0.48 V.*

FIGURE 13. *Measurement of corrosion rate by the polarization resistance technique.*

Given the linearity of the slope of the ΔE vs Δi curve, i_{corr} has been shown to be related to the inverse of this slope by the following equation:

$$i_{corr} = [\beta_a \beta_c/2.3 (\beta_a + \beta_c)] \Delta i/\Delta E \qquad (4)$$

where β_a and β_c are the anodic and cathodic Tafel slopes, respectively (Figure 13). It is generally accepted that the quantity $\beta_a \beta_c/2.3 (\beta_a + \beta_c)$ is a constant, B. Hence, i_{corr} will be given by the relationship

$$i_{corr} = B (\Delta i/\Delta E) \qquad (5)$$

with B being measured experimentally or estimated from experimental data. In general, corrosion rates determined by linear polarization have been shown to be in good agreement with corrosion rates obtained by weight-loss methods. A more recent appraisal, using mathematical, graphical, and computer methods has led to the conclusion that the assumption of linearity is sufficient for the technique to be valid in many practical corrosion systems. More details on this technique can be found in a review by Mansfeld,[39] which describes its historical evolution and applica-

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tions, as well as its limitations. The review also includes a compilation of typical B values for various metal/environment combinations.

In practical situations, electrochemical systems are often more complex than the simple model assumed by the polarization resistance method. Metal surfaces immersed in natural aqueous electrolytes are often covered (or at least partially covered) with organic and biological films. Under these conditions, the interface behaves more like a combination of resistance and capacitance in parallel than like a pure resistor, and there may be an uncompensated IR drop through the biofilm. The presence of biofilms in any MIC situation further complicates the situation by the introduction of additional electrochemical reactions and adsorptive processes, which can lead to nonlinear polarization behavior. Even so, the polarization resistance (in units of ohms) can be found, as long as a sufficiently slow (determined by the slowest RC time-constant) polarization scan rate is used to maintain steady-state conditions, and a correction can be made for solution (or biofilm) resistance.

The polarization resistance technique is most useful for systems undergoing uniform corrosion. Patchy biofilms and localized colonization give rise to localized biochemical reactions and to anodes and cathodes that are fixed in space and stable in time,[39] as opposed to the randomly spaced and mobile oxidation and reduction reactions required by uniform corrosion. Under these conditions, the calculated polarization resistance value is correct but the anode and cathode areas are unknown, so that one does not know how to determine the current density. The equations from which i_{corr} is calculated are not well defined if either β_a or β_c approaches zero or infinity. This makes it difficult to use on active-passive metals for which β_a is very large in the passive region, or in diffusion-limited situations in which β_c often approaches $-\infty$. Despite these difficulties, several papers have been published during the last few years[40-42] using this method to assess different microbial effects on corrosion rates.

The polarization resistance method can be useful for monitoring corrosion rates and detecting when a change in the rate occurs. The problem is that it is not usually possible to determine from the polarization resistance measurements alone why the rate changed, only that it did. Moreover, if biofilms or localized corrosion are present, the polarization resistance method will reveal that something is happening, but may not give an accurate measure of the corrosion rate.

ELECTRICAL RESISTANCE PROBES

The electrical resistance method is widely used as an industrial corrosion monitoring technique.[43] A thin metallic wire or strip sensing element (or probe) is inserted into the corrosive medium, and its electrical resistance is monitored with time. The electrical resistance of the probe is inversely proportional to the cross-sectional area and directly proportional to temperature. Thus, at constant temperature, corrosion of the probe, which causes a decrease in cross-sectional area, can be monitored by periodically measuring the electrical resistance. The average corrosion rate is then determined from the increase in resistance between any two readings. The corrosion rate can be determined by this method over very short times, but not instantaneously, and the environment does not have to be an electrolyte.

The electrical resistance method is excellent for indicating a change in the general corrosion rate, but the results are harder to interpret in the presence of localized forms of corrosion, such as pitting, crevice corrosion, stress corrosion cracking, and corrosion fatigue, which take place with very little mass loss. Workers have attempted to correlate characteristic jumps in resistance with localized forms of corrosion, but with only limited success.

An electrical resistance probe will indicate very little corrosion if the corrosion products have an electrical conductivity approaching that of the lost metal or if an electrically conducting film forms on the metal surface. MIC usually produces localized forms of corrosion, and it is sometimes associated with conductive corrosion product films. Therefore, in cases of known or suspected MIC, the electrical resistance method should be used only with caution, and in conjunction with other methods.

SPLIT-CELL MEASUREMENTS

An electrochemical technique recently applied[44] to the assessment of microbial activity in corrosion processes involves the use of a split cell similar to those used for many years in galvanic couple studies and as biological fuel cells.[45] Generally, this type of cell contains two similar compartments filled with the same electrolyte and each containing an identical metal electrode. One of these electrode half-cells is sterile and the other is inoculated with the microorganisms under study. The external electric circuit is completed through a zero-resistance microammeter, while the contact between the solutions in the two chambers is made across a semipermeable membrane. In this way, the current obtained under short-circuit conditions is considered as a measure of the biological effect on the inoculated electrode.

Inherent in this method is the assumption that the two electrodes can be made identical and that there would be no current flow as long as both half-cells were maintained in the sterile condition. This may be a reasonable assumption in the case of steady-state uniform corrosion, or for stable passivity where neither electrode undergoes potential fluctuations in the absence of the microorganisms. It is probably not valid for systems such as the 300 series stainless steels in seawater. In this latter case, the potentials of the two electrodes are sufficiently variable that currents could flow in either direction whether or not microorganisms are present. In such systems, interpretation of the data from split-cell experiments is not straightforward.

An advantage of this experimental technique is that, under ideal conditions, it enables one to experimentally separate areas of sterile, bare metal surface from those of the same metal covered with a microbial film (or at least in the presence of the microbes). The corrosion currents, if any, flowing between these separated areas can then be measured. The method, however, does not separate the anodes and cathodes of local action or microcells, but only measures the effect of coupling. Thus, it is not a simple matter to relate the data obtained from this method to MIC on real structures covered with a spotty biofilm or with discrete biodeposits.

The main utility of the method is in research, where it is desirable to demonstrate various effects that microorganisms can have on corrosion. Recently, this type of device has been used successfully to study the effects of: (1) a marine *Pseudomonas* on corrosion of copper,[46] (2) an obligate thermophilic filamentous bacterium on the corrosion of nickel,[47] (3) an iron-oxidizing stalked bacterium on the corrosion of mild steel,[44] and (4) an aerobic acetic acid producing bacterium on the cathodic depolarization of stainless steel.[48]

ALTERNATING CURRENT METHODS

Direct current techniques assess the overall corrosion process occurring at a metal surface, but treat the metal/solution interface as if it were a pure resistor. Problems of accuracy and reproducibility frequently encountered in the application of direct current methods have led to an increasing use of electrochemical impedance spectroscopy (EIS). The rapid development of commercially available instrumentation currently allows measurements

to be taken over a wide range of frequencies from 10^{-3} to above 10^3 Hz. The theory and practice of EIS techniques have recently been reviewed by Silverman.[43]

The EIS technique measures not only the resistive but also the capacitive and possibly the inductive components of the over- all interfacial impedance, therefore being particularly useful in the presence of nonconducting and semiconducting surface films such as organic paints and many metal oxide films. Many of the organic and microbiological films that adsorb on surfaces immersed in nat- ural aqueous environments are nonconducting, and EIS techniques are potentially useful in their presence. EIS techniques are most helpful, and easiest to interpret for metal–electrolyte sys- tems involving continuous thin films and low solution conductivity. Some caution should, therefore, be exercised in data interpretation from MIC systems because the adsorbed organic and biological films tend to provide spotty, rather than continuous surface cover- age, and these films can vary widely in thickness. It is rare to find a biofilm that is both thin and continuous. Biofilms that meet the criterion of being thin are also usually quite spotty, while those that have become nearly continuous are also thick. Nevertheless, EIS should provide useful information on biofilm-covered electrodes and may be helpful in assessing the degree of coverage similarly to its use in determining the porosity of coatings.[50]

EIS techniques are able to distinguish between electrochemi- cal reactions based on their relaxation times. A given electrochem- ical reaction will only respond to an alternating current signal whose period is longer than the characteristic time for the rate lim- iting step for that reaction to occur across the interface. The evalu- ation of the impedance spectrum of an electrode over a wide range of frequencies can then be used to distinguish among the various processes taking place at the interface between the metal and the electrolyte or between the metal and a film or coating. One of the most successful uses of EIS has been for assessing the performance of various types of organic coating materials. Per- haps the most serious impediment to the widespread use of EIS for corrosion studies is the complexity and cost of the instrumenta- tion needed and the sophisticated electrochemical expertise re- quired for detailed data analysis.

In relation to using EIS in MIC research, there are several cautions that should be observed:

(1) The interpretation of EIS data depends largely on the de- velopment of equivalent electrical circuits for modeling of the solid/electrolyte interface. These equivalent circuits are difficult to formulate for complex interfaces involving partial coverage by microbial films.

(2) The combination of microbial film and corrosion products often encountered in MIC causes the impedance to be- come very high at low frequencies, thus requiring extra- polations.

(3) Microbial films are not static like paint films or even metal oxide films after reaching steady state in a given electro- lyte. Rather, microbial films are dynamic entities, within which changes are continually occurring under the influ- ence of the organism's metabolism. Such changes can cause short-term fluctuations in the electrochemistry at the metal/film interface, causing localized attack under the film that is not easily detected.

(4) The period of these fluctuations can be shorter than the time necessary to gather EIS data when using a full-fre- quency sweep, meaning that all frequencies of the ap- plied signal may not be responding to the same electro- chemical conditions.[51]

Several papers recently published[12,42,52,53] include the use of this technique in MIC research. However, a detailed description of the results as well as the fundamentals of the EIS method is be- yond the scope of this paper. For further discussion on the details of the technique, the reader is referred to the literature.[54,55]

ELECTROCHEMICAL NOISE

In the electrochemical noise technique, the metal specimen to be tested is connected through a resistor and a capacitor to an inert electrode such as platinum. Microvolt level changes in poten- tial are then measured across the resistor with a sensitive voltme- ter connected to a recorder,[56] or more recently, to a computer. Theoretically, the higher the frequency and amplitude of the poten- tial fluctuations observed during corrosion, the greater the number of events participating in the corrosion process and thus, the higher the corrosion rate. By using this technique, it has been ad- vocated recently that it is possible to detect the onset of localized corrosion, distinguish between localized and generalized corrosion, and specify the type of the former, distinguishing between crevice or pitting attack.[57] In a variation of this technique, the current fluc- tuations between two nominally identical specimens provide a record of electrochemical noise, the structure of which has been correlated with localized corrosion.[58]

Electrochemical noise techniques have been applied to the study of anaerobic corrosion of iron by SRB.[59] Potential fluctua- tions accompanying the breakdown of an SRB produced iron sul- fide film on iron have been recorded in the laboratory. Such fluctu- ations have also been recorded from steel pipelines in the field,[60] and it may be possible to correlate this data with areas of anaero- bic corrosion of the pipeline. Another application of electrochemi- cal noise techniques has been to the study of SRB effects in the corrosion of reinforced concrete.[53] A recent study of noise analysis of pure aluminum in chloride media shows that noise analysis can be used to study pitting corrosion under different conditions.[61] Be- cause of the importance of pitting attack in MIC, electrochemical noise techniques may play an important role in the study of micro- bial effects on corrosion in the future.

SUMMARY

▶ Microbial colonization of metals and alloys can drastically alter their corrosion behavior and resistance to passive film breakdown by causing localized changes in the type and concentrations of ions, pH, and oxygen levels. In addition, diffusional barriers to the transport of chemical species at the metal/solution interface can be introduced by microbial EPS production. These effects result in localized changes in passive film composition and type of corro- sion products, and may result in changes in the measured electro- chemical parameters used in the experimental methods discussed above.

▶ Electrochemical measurements can be made under MIC condi- tions in both the laboratory and the field. However, all electrochemical methods are averaging techniques that work best when the chemical and electrochemical conditions on the metal surface are uniform and at steady state. By their very nature, bio- films tend to create conditions that are non-uniform and variable. Moreover, the chemical and electrochemical conditions at the me- tal/biofilm interface usually bear little resemblance to those in the bulk electrolyte or at the metal/electrolyte interface in the absence of the biofilm. In addition, the large deviations from steady state required by some of the techniques (e.g., potentiodynamic polar- ization) can produce conditions at the interface that alter the activi- ties of, or even kill the organisms. Therefore, although each of the electrochemical techniques discussed above has some applicabil- ity in MIC research, each also has limitations, and none of them should be used without an appreciation of those limitations and a reluctance to overinterpret the data.

▶ It is becoming increasingly obvious that traditional concepts of the inorganic physical chemistry and electrochemistry at "organic-free" metal/solution interfaces are inadequate when dealing with biologically "conditioned" metal surfaces. Whenever possible, investigations on MIC, whether basic research to study mechanisms or applied research to solve an industrial problem, should use multiple methods. The careful use of several electrochemical methods should be coupled when possible with visual inspection, weight-loss measurements, modern surface analysis techniques, and an adequate characterization of the type(s) of microorganisms involved, their interactions, and the effects of their metabolic activities and products. Evaluation of such data by teams of investigators knowledgeable in both corrosion and microbiology will eventually give us a better overall understanding of the microbial contribution to corrosion processes in a variety of environments.

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